Communications
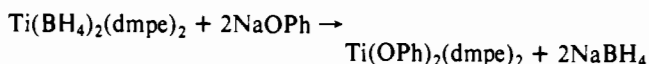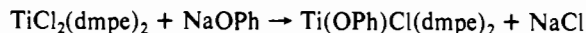
On the π-Donor Ability of Early Transition Metals: Evidence That Trialkylphosphines Can Engage in π-Back-Bonding and X-ray Structure of the Titanium(II) Phenoxide Ti(OPh)₂(dmpe)₂

We have recently proposed the idea that the early transition metals in their lower oxidation states are unusually strong π-donors and that this phenomenon to a large degree governs the characteristic chemistry of these elements.[1-3] We now show how this effect can explain unexpected spin state changes in a series of titanium(II) phosphine complexes. We also describe the synthesis of the first well-characterized titanium(II) aryloxide and a description of its bonding.

Interaction of *trans*-TiCl₂(dmpe)₂[4] (dmpe = 1,2-bis(dimethylphosphino)ethane) with sodium phenoxide in diethyl ether followed by filtration and cooling affords red crystals of the titanium(II) phenoxide complex *trans*-Ti(OPh)Cl(dmpe)₂.[5] The monophenoxide complex is isolated even in the presence of excess NaOPh. However, treatment of the tetrahydroborate complex *trans*-Ti(BH₄)₂(dmpe)₂[6] with 2 equiv of NaOPh in tetrahydrofuran results in the replacement of both BH₄⁻ groups and formation of the bis(phenoxide) complex *trans*-Ti(OPh)₂(dmpe)₂.[7]

$$\text{TiCl}_2(\text{dmpe})_2 + \text{NaOPh} \rightarrow \text{Ti(OPh)Cl(dmpe)}_2 + \text{NaCl}$$

$$\text{Ti(BH}_4)_2(\text{dmpe})_2 + 2\text{NaOPh} \rightarrow$$
$$\text{Ti(OPh)}_2(\text{dmpe})_2 + 2\text{NaBH}_4$$

Unlike TiCl₂(dmpe)₂ and Ti(BH₄)₂(dmpe)₂, which are paramagnetic d² species, the two phenoxide complexes are *diamagnetic*. Along with the previously reported methyl complex *trans*-TiMe₂(dmpe)₂,[8] which is also diamagnetic, these are the only examples of octahedral complexes of a first-row transition metal that exhibit spin pairing within the t_{2g} (or pseudo-t_{2g}) manifold.

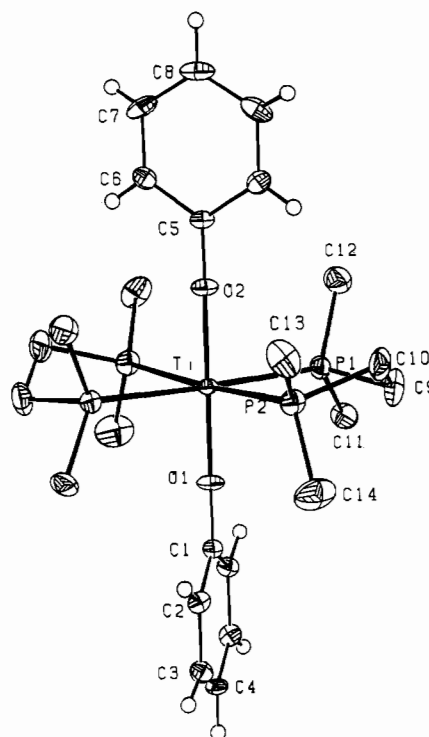The titanium center in Ti(OPh)₂(dmpe)₂ adopts an octahedral coordination environment (Figure 1).[9] The average Ti–P distance

Figure 1. Molecular structure of Ti(OPh)₂(dmpe)₂, with atoms shown with 35% probability surfaces. The molecule resides on a crystallographic 2-fold axis that passes through C8, C5, O2, Ti, O1, C1, and C4. Selected distances (Å) and angles (deg): Ti–O1 = 1.891 (6), Ti–O2 = 1.930 (6), Ti–P1 = 2.519 (2), Ti–P2 = 2.511 (2); P1–Ti–P1' = 177.80 (9), P1–Ti–P2 = 78.79 (5), P1–Ti–P2' = 101.13 (5), P2–Ti–P2' = 175.78 (9), P1–Ti–O1 = 91.10 (5), P1–Ti–O2 = 88.90 (5), P2–Ti–O1 = 92.11 (5), P2–Ti–O2 = 87.89 (5), O1–Ti–O2 = 180, Ti–O1–C1 = 180, Ti–O2–C5 = 180.

of 2.515 (2) Å is essentially identical with the Ti–P distance of 2.514 (1) Å in diamagnetic TiMe₂(dmpe)₂,[8] but is significantly shorter than the 2.586 (5)–2.626 (1) Å distances in the high-spin species TiCl₂(dmpe)₂[4] and Ti(BH₄)₂(dmpe)₂.[6] The average Ti–O distance in Ti(OPh)₂(dmpe)₂ of 1.911 (6) Å is somewhat longer than those of 1.807 (8) to 1.891 (7) Å in titanium(III) aryl-

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(5) Anal. Calcd for C₁₈H₃₇ClOP₄Ti: C, 45.4; H, 7.82; Cl, 7.44; Ti, 10.1. Found: C, 46.0; H, 7.83; Cl, 6.11; Ti, 10.0. ¹H NMR (PhMe-*d*₈, 25 °C, 360 MHz): δ 6.87 (t, J_{HH} = 7.2 Hz, *m*-H), 6.51 (t, J_{HH} = 7.2 Hz, *p*-H), 5.91 (d, J_{HH} = 7.2 Hz, *o*-H), 1.58 (br s, PCH₂), 1.50 (br s, PCH₂), 1.46 (s, PMe₂), 1.27 (s, PMe₂). ³¹P{¹H} NMR (PhMe-*d*₈, 25 °C, 121 MHz): δ 51.7 (s).
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(7) Anal. Calcd for C₂₄H₄₂O₂P₄Ti: C, 53.9; H, 7.92; Ti, 8.96. Found: C, 54.2; H, 7.97; Ti, 9.13. ¹H NMR (PhMe-*d*₈, 80 °C, 360 MHz): δ 6.92 (t, J_{HH} = 7.2 Hz, *m*-H), 6.49 (t, J_{HH} = 7.2 Hz, *p*-H), 6.02 (d, J_{HH} = 7.2 Hz, *o*-H), 1.43 (br s, PCH₂), 1.29 (br s, PMe₂). Rotation of the phenoxide groups is fast on the NMR time scale above 40 °C. ³¹P{¹H} NMR (C₆D₆, 25 °C, 121 MHz): δ 50.0 (s).
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(9) Crystal data for **2** (*T* = 198 K): space group *C2/c*, with *a* = 9.509 (1) Å, *b* = 20.888 (4) Å, *c* = 14.430 (4) Å, *β* = 92.80 (2)°, and *V* = 2683 (2) Å³; *Z* = 4; R_F = 0.051, R_{wF} = 0.070 for 228 variables and 1431 unique data for which *I* > 2.58σ(*I*). Hydrogen atoms were located in the Fourier difference maps, and their locations were independently refined with separate isotropic thermal parameters. An Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα X-rays (λ = 0.71073 Å), was used in the ω/θ scan mode to collect 2415 total reflections with 2.0 ≤ 2θ ≤ 50.0° in one quadrant (±*h*,+*k*,−*l*) on a 0.2 × 0.2 × 0.4 mm crystal. The 2143 unique reflections gave an agreement factor R_i = 0.017.

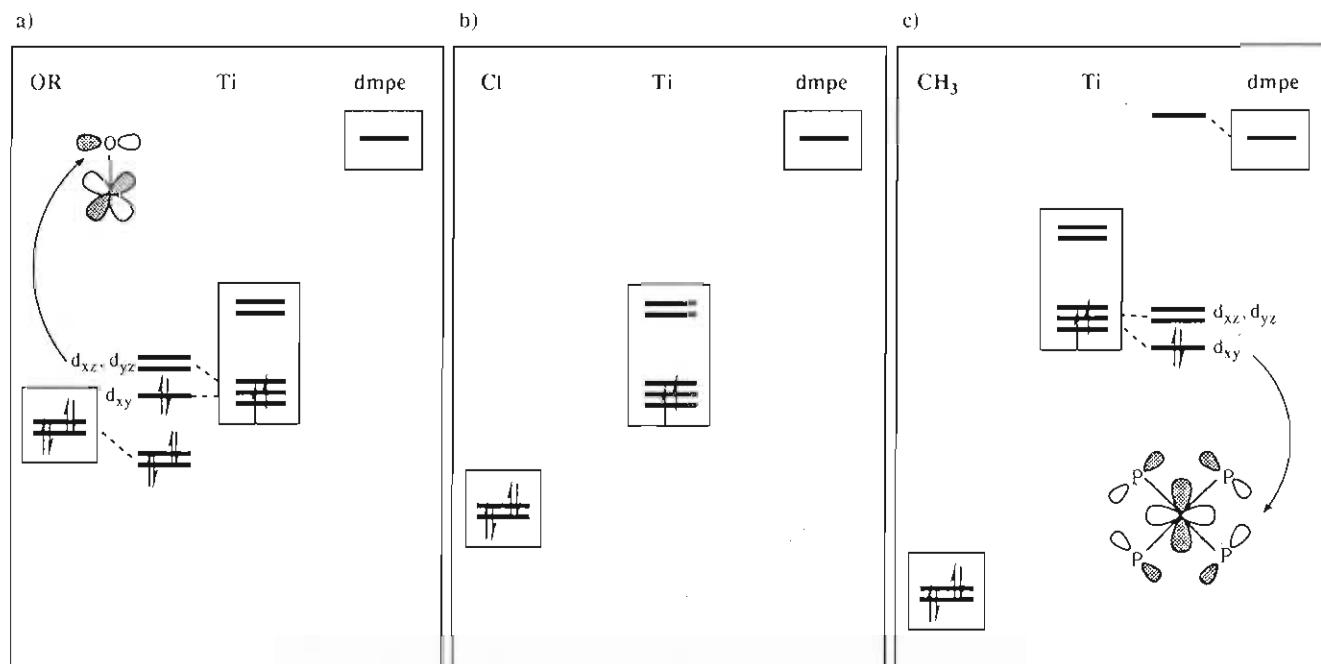**Figure 2.** Molecular orbital scheme for (a) $Ti(OPh)_2(dmpe)_2$ showing splitting of t_{2g} orbitals due to (PhO) → M π-donation, (b) $TiCl_2(dmpe)_2$, and (c) $TiMe_2(dmpe)_2$ showing splitting of t_{2g} orbitals due to M → (PR_3) π-donation.

oxides,[10-14] as expected from the larger radius of Ti^{II}. The planes of the two phenoxide groups are mutually orthogonal; the overall geometry of $Ti(OPh)_2(dmpe)_2$ is similar to that of the previously reported d^2 niobium(III) aryloxide cation $[Nb(O-2,6-(i-Pr)_2C_6H_3)_2(dmpe)_2^+]$.[15]

The d^2 complexes of $TiX_2(dmpe)_2$ have forced us to reevaluate our view of the bonding in trialkylphosphine complexes of the early transition metals. To date, there has been little compelling evidence to support the idea that trialkylphosphines can engage in strong π-back-bonding with transition metals. Of the few physical methods that can distinguish σ- from π-bonding effects, PES studies[16-18] suggest that trialkylphosphines have bonding properties that are similar to those of trialkylamines[19] and are therefore weak π-acceptors at best.[20,21] Other evidence that trialkylphosphines can serve as π-acceptors is that metal–phosphorus bond lengths often increase slightly upon oxidation of the metal center.[22-27]

However, this effect gauges only indirectly the degree of π-back-bonding. Finally, there are some theoretical studies of the π-accepting ability of phosphorus ligands.[28,29] However, none of these studies yields direct evidence that the energies of metal-based orbitals of π-symmetry are strongly perturbed by bonding with trialkylphosphine ligands. The $TiX_2(dmpe)_2$ compounds provide such evidence.

The $TiX_2(dmpe)_2$ complexes can be divided into two classes according to their spin state: the two phenoxide complexes and $TiMe_2(dmpe)_2$ are diamagnetic, while the chloride, bromide,[30] iodide,[30] and tetrahydroborate analogues are paramagnetic with two unpaired electrons. These spin states can be understood as follows. In a D_{4h} ligand field, the degeneracy of the t_{2g} orbitals will be broken to yield orbitals of e_g (d_{xz}, d_{yz}) and b_{2g} (d_{xy}) symmetry.[31] The energy difference between the e_g and b_{2g} orbitals will be small unless (1) the axial X groups are strong π-donors,[32] or (2) the equatorial dmpe ligands are strong π-acceptors. Apparently, neither situation pertains in the $TiX_2(dmpe)_2$ complexes with X = Cl, Br, I, or BH_4 (Figure 2b), which must have small e_g–b_{2g} splittings to account for their paramagnetism. In contrast, the diamagnetism of the phenoxide complexes can be attributed to the first effect (Figure 2a), since aryloxides are better π-donors than halides. The orthogonal orientation of the two phenoxide groups in $Ti(OPh)_2(dmpe)_2$ also supports this view.[15]

However, the methyl groups in $TiMe_2(dmpe)_2$ are certainly *not* strong π-donors despite our earlier suggestion.[8] It is clear from PES studies[33] of other transition-metal alkyls that the filled C–H σ-bonding orbitals of local e symmetry (constructed from the carbon p_x and p_y orbitals) are far too low in energy to interact strongly with the titanium d_{xz} and d_{yz} orbitals. Instead, we propose that the phosphine ligands are acting as strong π-acceptors. This

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(21) In contrast, many studies clearly provide convincing evidence that *aryl*phosphines can serve as strong π-acceptors.[16-20]

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(31) Although the idealized point symmetries of the $TiX_2(dmpe)_2$ molecules are actually D_{2h}, the D_{4h} symmetry labels more conveniently show the near-degeneracy of the d_{xz} and d_{yz} orbitals.

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is possible in part because the low effective nuclear charges Z_{eff} of the early transition elements make the d orbitals unusually high in energy. The energies of the d orbitals are raised even higher in $TiMe_2(dmpe)_2$ (but not in the halide or BH_4^- complexes) by the inductive effect of the strongly σ-donating Ti–Me groups. In other words, by acting as strong σ-donors, the methyl groups put more electron density on the titanium center, and the additional electron density helps to screen the nuclear charge.[34] In contrast, halide and BH_4^- groups are poor σ-donors and do not exert as strong an inductive effect. As a result, in $TiMe_2(dmpe)_2$ there is an unusually good match in the energies of the filled d orbitals and the empty P–C σ^* orbitals on the phosphine ligands. Because the b_{2g} (d_{xy}) orbital lies in the plane of the phosphine ligands, it can interact with four such σ^* orbitals, while the e_g (d_{xz} and d_{yz}) orbitals on Ti can interact with only two. Consequently, the b_{2g} orbital is preferentially stabilized (Figure 2c). The amount of π-overlap must be large, since the splitting between the b_{2g} and e_g orbitals is sufficient to cause pairing of the two d electrons of $TiMe_2(dmpe)_2$ in the b_{2g} orbital.[35]

These results add strength to the contention that early transition metals in their lower oxidation states are exceedingly strong π-donors,[1-3,36-38] and can engage in strong π-back-bonding even with normally poor π-acceptors such as trialkylphosphines. This view leads to some interesting predictions: for example, the strongest π-back-bonding between a carbonyl ligand and a transition metal should occur in compounds of low-valent hafnium[39-42] and *not* in compounds of the later transition elements as is commonly thought.[43]

Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for Ti-$(OPh)_2(dmpe)_2$ (4 pages); a table of final observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(43) **Note added in proof**: Detailed ab initio calculations have recently confirmed the importance of the low Z_{eff} and the inductive shielding effect of the Ti–Me groups in $TiMe_2(dmpe)_2$. However, the results suggest that the diffuse nature of the d orbitals and the resulting decreased electron–electron repulsions are largely responsible for the diamagnetism (Simpson, C. Q.; Hall, M. B.; Guest, M. F. Submitted for publication). We thank Professor Hall for sharing his results with us before publication.

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Excited-State Properties of Mononuclear and Binuclear Rhenium(I) Complexes

The spectroscopic and photophysical properties of oligonuclear complexes containing d^6 metals have received considerable attention of late, in part because of their potential utility in photochemical energy storage systems and as multielectron redox agents. In particular, multinuclear transition-metal-based systems containing ligand bridges have been utilized in a number of studies concerning electron- or energy-transfer reactions.[1-10] Rhenium(I) complexes are especially attractive in this regard, since they are readily synthesized, are chemically stable, and generally possess an extremely high quantum yield for emission.[7-13] However, some of the binuclear complexes of this type, such as the 2,2′-bipyrimidine-bridged compound prepared by Vogler and Kisslinger,[7] are virtually nonemissive. Although those authors suggested that population of a low-lying metal-to-metal charge-transfer excited state was responsible for the lack of luminescence, recent work in our laboratory[9] and elsewhere[5,10] indicates that the perturbation of the π^* orbital on the bridging ligand is of prime importance in determining the photophysical properties of such complexes. Tapolsky et al.[10] have exploited this effect to achieve an "electron/energy-transfer cascade" in the binuclear complex $[(bpy)(CO)_3Re(4,4′-bpy)Re(CO)_3(bpy)]^{2+}$, where 4,4′-bpy represents 4,4′-bipyridine and bpy = 2,2′-bipyridine. In this complex, the proximity of the Re → bpy and Re → 4,4′-bpy MLCT levels allows for control of the excited-state properties by variation of

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